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ON THE STABILITY OF THE S_8 MOLECULE AND THE STRUCTURE OF FIBROUS SULFUR

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Sulfur is unique among the elements in consisting in its standard state of octatomic molecules. It is interesting that the stability of the S_8 molecule can be understood by consideration of the forces determining the orientation around the sulfur-sulfur single bond.

Let us consider a molecule such as H_2S_2, in which each sulfur atom forms a single bond with the other sulfur atom and a single bond with another atom (hydrogen), and has in addition two unshared electron pairs in its outer shell. The bonds formed by the sulfur atoms involve mainly $3p$ orbitals, and one of the two unshared outer electron pairs occupies the third $3p$ orbital, the other unshared pair occupying essentially the $4s$ orbital. (A rough theoretical treatment which will be communicated later indicates that the bond orbitals have only about 1% s character.) The dihedral angle between the planes H—S—S and S—S—H is determined principally by the repulsion of $p\pi$ electrons. The repulsion between $p\pi$ electrons is at a maximum when the $p\pi$ orbitals of the two sulfur atoms are in the same plane, and falls to zero when these orbitals are in orthogonal planes. The energy of interaction of an unshared pair of $p\pi$ electrons on one atom and the similar unshared pair on the other atom in a coplanar $p\pi$ orbital is equal to -2α (the negative sign corresponding to repulsion, because α, the exchange integral occurring in the electron-pair bond theory, is itself negative), that between an unshared pair on one atom and a single bonding electron on another is $-\alpha$, and that between two bonding electrons is $-{}^1/_2\alpha$. Hence the total interaction energy of the $p\pi$ electrons in H_2S_2 varies from $-{}^5/_2\alpha$ for a planar configuration of the molecule (dihedral angle γ equal to 0° or 180°) to a minimum of -2α for $\gamma = 90°$. It is then to be predicted that the molecule H_2S_2 has a skew configuration, with the dihedral angle γ equal to approximately 90°. The configuration of this molecule has not been precisely de-

termined, although it is known not to be planar,[1] but the similar molecule hydrogen peroxide, H_2O_2, has been shown to have γ equal to approximately 106° in the crystal formed by hydrogen peroxide and urea[2] and a similar value in the pure substance.[3] (An explanation essentially equivalent to that given above was advanced by Penney and Sutherland to account for the skew configuration of hydrogen peroxide.[4]) Moreover, Guthrie has found, from a careful electron-diffraction investigation of sulfur monochloride, S_2Cl_2, that the dihedral angle in this molecule is equal to 92° ± 12°,[5] and the value of γ in dimethyltrisulfide has been found[6] to be approximately 106°. We accordingly conclude that the normal value of the dihedral angle γ for the sulfur-sulfur bond is in the neighborhood of 100°. The increase over the value 90° given by the simple theoretical treatment may be due to van der Waals repulsion of the non-bonded atoms and to other interactions, such as the electrostatic interactions of multipoles discussed recently by Lassettre and Dean.[7]

TABLE 1

VALUES OF THE DIHEDRAL ANGLE IN STAGGERED RING MOLECULES

NUMBER OF ATOMS IN RING	BOND ANGLE 90°	95°	100°	105°	110°	115°	120°
4	0°	.....	.....	.....	.....	.....	.....
6	90°	84°31′	77°52′	69°34′	58°41′	42°13′	0°
8	114°28′	111°0′	106°50′	102°6′	96°18′	89°10′	80°7′
10	128°10′	125°34′	122°32′	118°59′	114°48′	109°47′	103°39′
12	137°4′	134°57′	132°31′	129°41′	126°21′	122°24′	117°39′

In the molecule S_8, which has the staggered configuration, the S—S—S bond angle β has been found to be equal to 105° both in the orthorhombic crystal[8] and in the vapor.[9] The dihedral angle γ is not independently variable, but is determined by β; its value is 102°. This value is, according to the foregoing argument, close to the normal value, which minimizes the energy of the X—S—S—X group; and it is our thesis that the S_8 molecule is stable (relative to S_x, with $x \neq 8$) because its configuration leads to this value.

The relation between γ and β for symmetrical staggered rings (with point-group symmetry D_{nh}) containing n atoms (n even) is

$$\sin^2 \frac{\gamma}{2} = \frac{\cos(2\pi/n) + \cos\beta}{1 + \cos\beta}. \qquad (1)$$

In table 1 there are given values of γ for values of β between 90° and 120° and for n between 4 and 12. It is seen that for $\beta = 105°$, the value observed for sulfur, the minimum deviation from the normal value of γ, which we may take as 100°, occurs at $n = 8$, and amounts to about 2° as compared

with 19° for $n = 10$ and 30° for $n = 6$. Since the staggered configurations of the ring provide better approximation to the normal value of γ than do other configurations, this calculation gives an explanation of the stability of S_8 relative to other sulfur molecules. At higher temperatures sulfur vapor contains S_6 and S_2 as well as S_8. There is little doubt that the S_6 molecule is a staggered hexagonal ring. The difference in heat content of S_6 and S_8 has been evaluated from thermochemical data by Bichowsky and Rossini,[10] and found to be equal to 1.25 kcal./mole per sulfur-sulfur bond. The interaction energy of the $p\pi$ electrons is according to simple theory proportional to $\sin^2 \gamma$. On this assumption, and the assumptions that the bond angle β is the same in S_6 as in S_8 and that the normal value of γ is 100°, α can be evaluated as -9.8 kcal./mole. This value for α can be considered to be only a very rough one, inasmuch as other structural factors also without doubt contribute to the difference in energy of S_6 and S_8, but it is worth pointing out that the value is not unreasonable.

The standard state of selenium is a hexagonal crystalline state in which there are infinite spiral molecules of selenium atoms, with Se—Se—Se bond angle $\beta = 105°$. There also exists a less stable red crystalline state of selenium containing Se_8 molecules, and the vapor of selenium consists of Se_8 molecules, Se_6 molecules, and, at higher temperatures, Se_2 molecules. Bichowsky and Rossini give for the difference in energy of Se_6 and Se_8 the value 1.07 kcal./mole of Se—Se bonds, which corresponds to -8.4 kcal./mole for the resonance integral α.

The spiral molecules in the hexagonal crystals of selenium, and also those representing the standard state of tellurium, have a threefold axis. The relation between the dihedral angle γ and the bond angle β for a threefold spiral molecule is $\sin^2 \gamma = {}^1/_2 (1 - 2 \cos \beta)/(1 - \cos \beta)$, corresponding for the values 90°, 95°, 100°, 105°, 110°, 115° and 120° for β to the values 90°, 94°36′, 98°31′, 101°52′, 104°46′, 107°17′ and 109°28′ for γ. It is seen that for $\beta = 105°$, as observed for sulfur and selenium, the value of γ is nearly the same for the threefold spiral as for the 8-membered staggered ring. The greater stability of the crystals containing the threefold spiral for selenium and tellurium is presumably due to the strong interaction between neighboring molecules which is made evident in the semi-metallic properties of the crystals. For tellurium, with bond angle 102°, the value of γ is 100°.

The failure of oxygen to form a molecule such as O_8 is of course due to the greater stability of the multiple bonds in the O_2 molecule; this greater stability of multiple bonds over single bonds is characteristic of the first-row elements.

It is interesting that fibrous sulfur, made by stretching the rubbery form of sulfur obtained on cooling liquid sulfur-μ, seems not to contain spirals with a threefold axis, like the spirals in selenium and tellurium, but to have another structure. Meyer and Go[11] have reported that the unit of struc-

true of fibrous sulfur is monoclinic, with $a_0 = 26.4$ Å, $b_0 = 9.26$ Å, $c_0 = 12.32$ Å and $\beta = 79°15'$, and that it contains 112 atoms. The b axis is the fiber axis. These authors suggested that there are 14 chains with a repeating unit of eight atoms each in the unit, and proposed two alternative planar configurations for the chains. These planar configurations are, however, to be rejected, because they make the S—S—S—S dihedral angle equal to 0°,

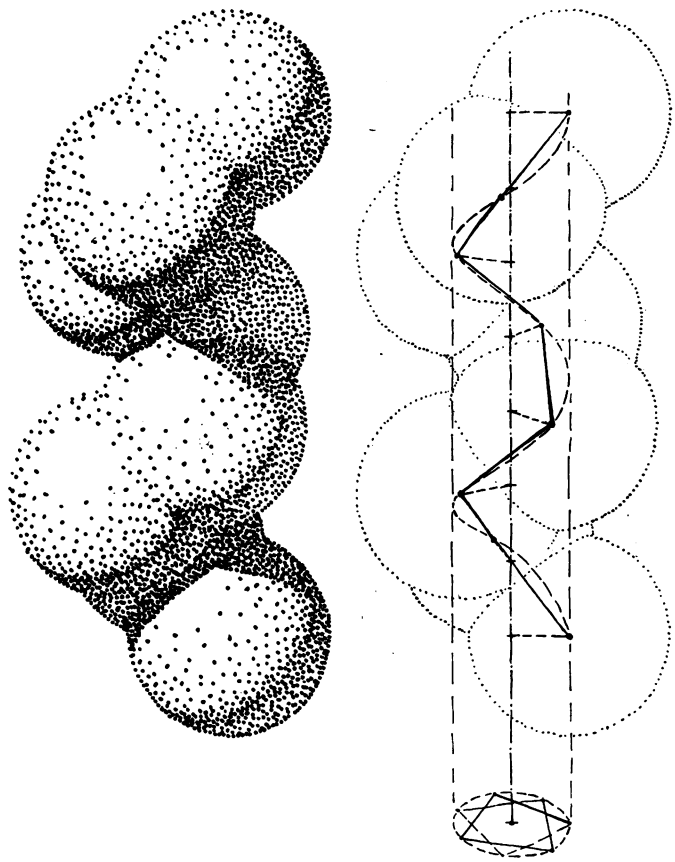

FIGURE 1

The seven-atom two-turn spiral proposed as the repeating unit in the chains of fibrous sulfur.

which corresponds to the minimum stability. It might indeed be expected that the sulfur atoms are arranged in a simple threefold spiral, with two turns in the unit distance b_0, as was tentatively suggested by Huggins.[12] This, however, leads to the value 109° for the S—S—S bond angle, which is unsatisfactory, and, moreover, the reported number of atoms in the unit is not a multiple of 6.

A conclusion about the probable structure can be reached from the assumption that the S—S distance and the S—S—S bond angle have the same values (2.08 Å and 105°) as in S_8. It is found that no spiral making a single turn in the identity distance b_0 is acceptable. A spiral making two turns in b_0 would be predicted, with the above parameters, to have b_0 = 8.89 Å for six atoms, 9.12 Å for seven and 8.49 Å for eight. Only the second of these is close enough to the observed value 9.26 Å to be indicated as correct; indeed, increasing the bond angle to 106° leads for the seven-atom two-turn spiral to exactly b_0 = 9.26 Å. The dihedral angle for this spiral is 76°, which is intermediate between the value for S_8 and that for S_6, and, through its derivation from the value corresponding to maximum stability, is compatible with the ease of conversion of fibrous sulfur into orthorhombic sulfur. The seven-atom chain unit explains the unusual occurrence of a multiple of seven atoms (112) in the unit of structure; the packing of chains is such as to lead to sixteen chains, parallel to b, per unit. Moreover, the fact that b_0 is 9.26 Å rather than approximately half so large is explained by the seven-atom spiral, which repeats only after seven atoms, whereas the six-atom and eight-atom spirals (with two turns) would repeat after a single turn. It is accordingly very likely that the structural unit of fibrous sulfur is the seven-atom two-turn spiral, shown in figure 1. The geometrical properties of the spiral are such that the distances $b_0 = 9.26 \pm 0.05$ Å and S—S $= 2.08 \pm 0.02$ Å determine the bond angle to be $106° \pm 1/2°$.

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